ABSTRACT

CHARACTERIZATION OF PITCHES FOR CARBON ANODES. M. B. Dell, Aluminum Company of America, Alcoa Research Laboratories, New Kensington, Pennsylvania

Pitches were analyzed for the usual determinations including coking value, C-I, C-II, and atomic C/H ratio. Relative aromaticities of the pitches were also measured by refractive index and sulfonation index of pitch distillates, C/H ratio of the carbon disulfide soluble phase, and infrared index. The relative aromaticities agreed quite well among themselves but did not correlate with the usual determinations. It was shown that the density and reactivity of carbon anodes varied with the aromaticity of the binder pitch as measured by infrared index.

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CHARACTERIZATION OF PITCHES FOR CARBON ANODES

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Numerous tests have been suggested for characterizing the binder pitches that are used in anodes for aluminum smelting. The commonly employed ones include softening point, ash content, coking value, and the amount of material insoluble in quinoline, benzene, or acetone. Some of these measure utility rather than quality. Softening point determines the minimum mixing temperature of the coke-pitch blend; ash content affects the purity of the aluminum. Other of these tests are indirect measures of aromaticity in the oil phase. Van Krevelen[8] has pointed out that aromatic compounds form coke more readily than non-aromatic compounds. Accordingly, the coking value of pitch is really an indirect measure of aromaticity. Similarly, for coke-oven pitches, a high C-I content shows that the pitch is highly cracked and more likely to have a high aromatic content.

Recently, new tests have been proposed to characterize binder pitches. Brückner and Huber[1] recommended solvent fractionation. Krylov et al[4] investigated the "free carbon" fraction. Martin and Nelson[6] suggested a modified coking value test and also[5] the use of specific gravity corrected for C-I. Charrette and Bischofberger[2] found a good correlation between compressive strength of a carbon anode, and the product of coking value and carbon-hydrogen ratio of the pitch binder. Montgomery and Goodspeed[7] discussed infrared spectroscopy of binder pitches using the KBr technique.

In the work reported here, binders representing different types of pitches were analyzed by the usual characterizations and by tests which measure their aromaticity. These latter tests comprised carbon-hydrogen ratio of the whole pitch, carbon-hydrogen ratio of the carbon disulfide-soluble phase, sulfonation index, refractive index, and infrared index. As will be shown, aromaticity of the binder pitch is important for carbon anodes used in aluminum smelting.

In comparing pitches by these tests, the composition of pitch should be kept in mind. Pitches consist of an insoluble phase suspended in an oil phase. Insoluble matter is derived chiefly from the soot formed during thermal cracking of tars from which pitches are produced, and from carry-over of the material being carbonized. The oil phase consists chiefly of hydrocarbons, sometimes with the presence of compounds containing oxygen, sulfur, or nitrogen. No single chemical compound predominates in the oil phase.

The amount of material insoluble in certain solvents is usually designated C-I when a good solvent such as carbon disulfide or quinoline is used. C-II designates the difference between the material insoluble in a poor solvent such as acetone or benzene and the C-I. Dickinson[3] demonstrated that the C-I fraction corresponds to the tar-insoluble matter, and that the C-II fraction contains the higher molecular weight substances of the oil phase.

PROCEDURE

Softening point was determined by the cube-in-air method, Barrett D-7.

Coking value was determined by method ASTM D-271 in which a 1-gm sample is heated to 950°C for seven minutes in a platinum crucible.

C-I. A one-half gm sample of the binder was digested in 10 ml of quinoline for 30 minutes at 70 to 80°C. The solution was filtered hot, washed with ten 5-ml portions of quinoline, and twice with benzene. The insoluble matter was weighed and reported as C-I.

C-II. One hundred ml of acetone were slowly added to a one-half gm sample of binder, then stirred and filtered with suction through a Royal Berlin Porcelain crucible, type 1A2. Insoluble matter was washed once with 10 ml of acetone, dried, weighed, and reported as C-I plus C-II. The C-II value was the difference between C-I and the acetone insoluble.

Sulfonation index and Refractive index - Each binder was distilled in a side-neck Church flask using the procedure of ASTM D-20. The 300-365°C fraction was retained for determination of both the sulfonation index and refractive index. Sulfonation index was determined by ASTM method D-872 as the ml of unsulfonated residue per 100 gm of distillate using 37N sulfuric acid. Refractive indices were determined at 25° for solutions in p-xylene containing 25 per cent distillate.

Atomic carbon/hydrogen ratio - C/H was calculated from the carbon and hydrogen content of the pitch, determined in a combustion train.

Atomic carbon/hydrogen ratio of the carbon disulfide soluble phase - Five gm of pitch were dissolved in 20 gm carbon disulfide, filtered through a medium sintered-glass filter, and washed four times with a total of 20 gm carbon disulfide. Carbon disulfide was evaporated from the combined filtrates in a warm Petri dish. Carbon and hydrogen were determined on the extract.

Infrared Index - Exactly 0.25 gm of pitch was dissolved in 10 ml of carbon disulfide and allowed to stant two hours; then the infrared spectrum of the supernatant liquid was determined, using a cell width of 0.50 mm in a Perkin-Elmer Model 112 Spectrometer. After correcting for the absorption of the solvent, the infrared index was taken as the ratio of the aliphatic transmittance at 3.4 microns divided by the aromatic transmittance at 3.3 microns. It was realized that absorption might be used instead of transmittance, but since the index is an arbitrary ratio, the transmittance was used because the calculations were somewhat simpler. Aliphatic and aromatic transmittances at other wave lengths could have been used, but they produce little change in the relative indices of a series of pitches.

DISCUSSION AND RESULTS

The importance of aromaticity of binders in determining the quality of carbon anodes is shown in Figure 1. With increasing aromaticity, the baked apparent density of the anode increases. At the same time, the reactivity of the anodes decreases. The reactivity was taken as the loss in weight on immersing a 1-in. cylinder of carbon, 1/2-in. long, for one-half hour in sodium sulfate at 980°C.

In Table I, results of the analytical determinations are tabulated for a variety of pitches. The pitches are arranged in decreasing order of infrared index with the most aromatic pitch at the top. The infrared index increases regularly with C/H of the carbon disulfide soluble phase. It is a particularly sensitive measure of pitch aromaticity at high C/H ratios.

The deceptiveness of C/H of the whole pitch, as a

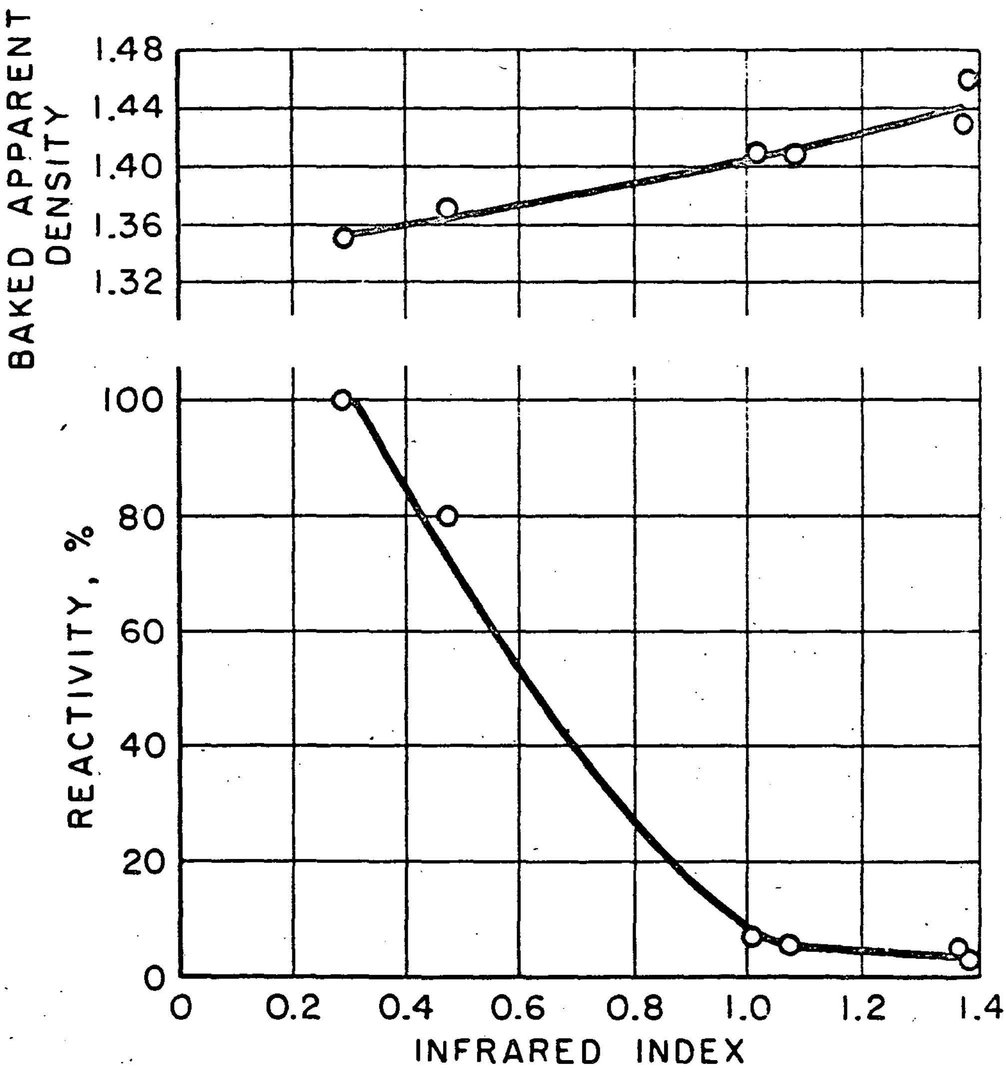

FIGURE I – EFFECT OF BINDER AROMATICITY ON PROPERTIES OF ANODES

TABLE I

CHARACTERIZATION OF PITCHES

Type	Softening Point °C	C-I %	C-II %	Coking Value	Coking Value Minus C-I	Atomic C/H Whole Pitch	Atomic C/H CS_2 Sol Phase	Sulfonation Index*	Refractive Index*	Infrared Index	Infrared Index*
Coke-oven A	109	16.5	33.0	44.1	27.6	1.91	1.77	0.0	1.5352	1.38	1.41
Coke-oven B	109	7.6	32.0	--	—	1.77	1.72	0.0	1.5376	1.37	1.38
Coke-oven C	110	13.7	30.8	44.2	30.5					1.35	
Horiz. retort	108	29.6	25.4	58.8	29.2	2.12	1.70			1.29	
European (?)	104	11.5	24.8	35.2	23.7	1.71	1.67			1.08	
Oil-gas A	116	13.3	37.2	42.8	29.5	1.74	1.59	2.2	1.5279	1.01	0.61
Water-gas	115	17.4	33.5	54.4	37.0	1.66	1.49	4.7	1.5298	0.94	0.59
Oil-gas B	114	17.0	27.1	50.7	33.7					0.83	
Low Temp.	87	0.2	4.6	11.1	10.9	1.15				0.47	
Lignite	--	2.8				0.81			1.5000	0.15	
Gilsonite	147	0.0	90.5	17.2	17.2	0.77	0.75			0.05	

*These determinations were made on the 300-365° distillate.

measure of aromaticity, is illustrated by the horizontal retort pitch where C/H of the whole pitch did not correspond with infrared index or the C/H of the carbon disulfide soluble phase. This is explained by the fact that the large amount of C-I having a high carbon content in this pitch tended to counteract the high hydrogen content of the oil phase.

The refractive index of the distillate fraction in p-xylene gave values that were somewhat indicative of the relative aromaticity of the pitch, but the results did not agree as well with the infrared index of the C/H of the soluble phase.

The sulfonation index of the distillate fractions agreed quite well with C/H ratio. The determination, however, is difficult to perform, and the test lacks sensitivity. The infrared indices of the 300-365°C distillate fractions correlated quite well with the infrared C/H indices of the whole pitch. This is understandable because in the infrared index determination the spectrum is only that of the oil phase of the pitch.

The traditional tests, C-I, C-II, and the coking value did not correlate with aromaticity as measured by infrared index or C/H of the soluble phase. The C-I phase of the pitch can have many different sources, and its amount does not necessarily measure aromaticity of pitch. While C-I, C-II, and coking value make good control tests for checking the uniformity of different shipments of pitch, their usefulness in evaluating new pitches is quite limited. The coking value, while it is in part a measure of the aromaticity of the pitch, is also affected by the insoluble content of the pitch. For example, the horizontal retort pitch that had a relatively low infrared index had a high coking value. Apparently this high coking value was mainly due to the high C-I content, which on carbonization goes almost entirely to form coke.

The coking value minus C-I, which has sometimes been suggested as a characterization factor for pitches, again shows no correlation with the aromaticity of the pitches as determined by infrared index or C/H of the carbon disulfide-soluble phase.

CONCLUSIONS

The quality of carbon anodes is related directly to the aromaticity of the binder pitch. The usual tests for pitches such as C-I, C-II, and coking value do not correlate with aromaticity.

The more useful characterizations for aromaticity include the C/H of the carbon disulfide soluble phase, sulfonation index, and infrared index of the whole pitch and the distillate fraction. Of these, the one that is most quickly determined is the infrared index of the whole pitch. The determination requires less than half an hour. Such a test should find wide application in laboratories that are called upon to examine numerous types of pitches.

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